A Robust Materials Preparation Technique Based on Novel Sol-gel Methodology

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UCRL–POST–206050

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

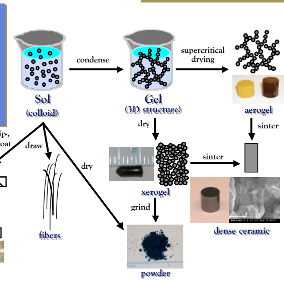
Introduction

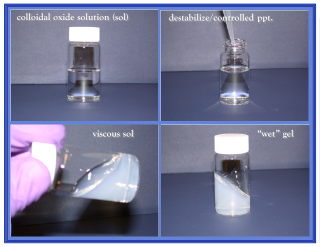
New, robust, and highly applicable materials preparation and processing techniques are invaluable for the advancement of materials chemistry. New preparation techniques are especially valuable due to the difficulty often experienced when trying to merge two or more phases into a single material on the molecular- or nano-scale. Current methodologies for achieving these goals can be highly variable as well as costly due to the myriad of synthetic and processing techniques available for many systems. These challenges are further compounded by the need for compatible and stable precursors, which are often difficult to handle, in order to merge two or more chemical systems into a single material.

Recently we have demonstrated a novel approach to the sol-gel synthesis of metal-oxide materials and material precursors. Though the compositions and applications of these materials have proven to be extremely diverse, the preparation methodology has remained constant through the use of a new concept in sol-gel chemistry. This new methodology takes advantage of recent breakthroughs in the use of organic proton scavenging agents to produce metal oxide precursors. These materials can be heat treated or easily processed into the desired materials. It is believed that the high degree of precursor mixing achieved by this method allows for easy transformations into desired crystalline phases, highly doped materials, and/or well-dispersed composites. In all of the demonstrated cases, the synthetic procedures used for the preparation have been robust and simpler than those currently proposed in the literature. Examples of composite materials prepared by this methodology include scintillators, novel ceramic precursors, laser materials, organic/inorganic interpenetrating networks, and nano-structured energetic composites. The starting materials were inexpensive, common metal salts (Cl^-, NO_3^-, etc.) that were processed in water or ethanol under ambient conditions. The general preparation method, processing of materials, and characterization of the wide variety of compositions prepared will be presented.

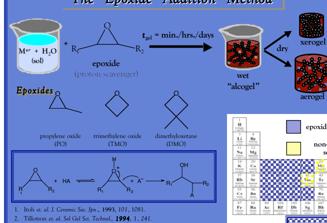
The Sol-Gel Methodology

- Cast complex shapes (eliminate machining)
- Low temp. processing
- No sophisticated lab equipment or conditions needed (<$$)
- *Amenable to nanocomposite synthesis*

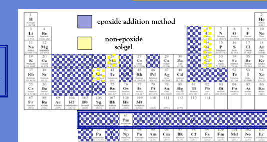




The Epoxide Addition Method



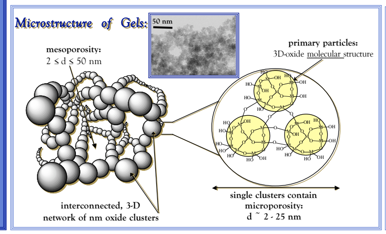
The epoxide addition method uses common metal salts as oxide precursors. The addition of an organic epoxide establishes a uniform pH gradient in the sol via a ring opening reaction, that induces oxide formation and gelation. A large degree of control over the gelation process can be maintained by the epoxide used.



1. Itoh et. al. J. Ceramic Soc. Jpn., 1993, 101, 1081.
2. Tillotson et. al. J. Sol Gel Sci. Technol., 1994, 1, 241.
3. Gash, A. E. et. al. Chem. Mater. 2001, 13, 999.
4. Gash, A. E. et. al. J. Non-Cryst. Solids, 2001, 285, 22.
5. Clapsaddle, B. J. et. al. J. Non-Cryst. Solids 2003, 331, 190.
6. Clapsaddle, B. J. et. al. J. Non-Cryst. Solids, 2004, in press.

* Seih, D. J.; Park, T. J.; Kim, W. J.; Hong, L. K. J. Power Sources 2003, 117, 1-6.

Microstructure of Gels:



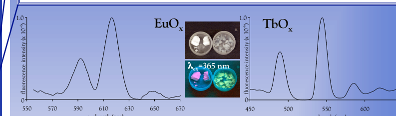
The epoxide addition method has several advantages over traditional, alkoxide sol-gel chemistry. Whereas metal alkoxides are often unstable and difficult to handle, the common metal salts used in the epoxide addition method are air stable and easily adapted to the synthetic conditions. Furthermore, alkoxide chemistry often requires a different set of reaction conditions for each metal-alkoxide system. The epoxide addition method is general to a large variety of transition and main group metals with little to no variation in synthetic conditions.

Crystalline and Doped Materials

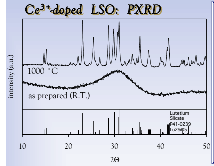
Lanthanide oxide based materials

One unique aspect of the epoxide addition method is the ability to form nano-particulate oxide materials of the entire lanthanide series. Lanthanide oxides (LnO_x) are useful dopants in a large variety of materials and are extremely useful for their fluorescent properties. This is the first reported procedure for synthesis of these materials by a single method amenable to bulk production of a large variety of pure LnO_x and LnO_x-containing materials.

Clapsaddle, B. J. *et. al.* *To be submitted to Chem. Mater.* 2004.

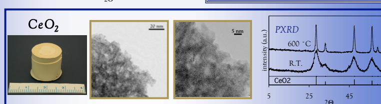


Ce^{3+}-doped LSO: PXRD



Lutetium oxyorthosilicate (Lu_2SiO_5; LSO) is a known **x-ray scintillator** when doped with various lanthanide ions (Ce^{3+}, Eu^{3+}, Tb^{3+}, etc.). LSO and Ln^{3+}-doped LSO can be prepared using the same method discussed below/left for the preparation of M-Si mixed oxides. Subsequent heat treatment results in the crystalline LSO materials which display strong fluorescence in the visible region.

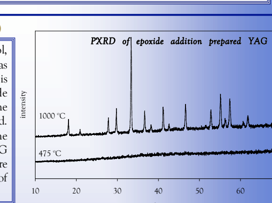
CeO_2



Using the epoxide addition method, nano-crystalline cerium (IV) oxide can be made without any heat treatment. CeO_2 is commonly used in hydrogen storage materials and catalysis.

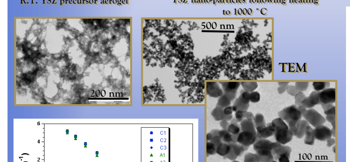
Yttrium-Aluminum Garnet ($Y_3Al_5O_{12}$; YAG)

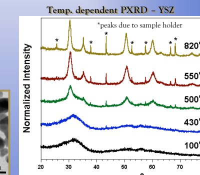
By mixing two or more metal salts in the initial sol, mixed oxide materials can be prepared as easily as monoxide materials. Since stoichiometry is controlled during the initial mixing of the oxide precursors, precise control over composition of the mixed oxide materials is easily controlled. Subsequent heat treatment thus results in the desired crystalline composition. In this case, YAG can be formed. YAG and Ln^{3+}–doped YAG are common lasing materials used for a large variety of laser applications.

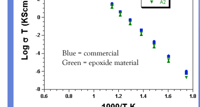


Fuel Cell Materials: YSZ

Yttria stabilized zirconia (YSZ) is an important material in hydrogen fuel cell electrodes. YSZ is an example of a doped material (YSZ=Y-doped ZrO_2) and demonstrates the usefulness of the epoxide addition method for preparing doped oxide materials. (Data courtesy of Chris N. Chervin and Prof. Susan Kauzlarich, U.C. Davis/LLNL Collaboration)







YSZ prepared from an aerogel with the desired stoichiometry begins to crystallize into the desired phase of ZrO_2 at ~ 500 °C (above right). Remarkably, the material remains nano-particulate even at temperatures up to 1000 °C (above left). When pressed into a pellet, the material shows similar conductivity data to that of commercially available YSZ powder (left).

M–Si Mixed Oxide Composites

Metal-silicon mixed oxide materials have a variety of applications including heterogeneous catalysis, magnetic materials, environmental remediation, and energetic materials. The epoxide addition method has resulted in M-Si mixed oxide systems in which the metal oxide is the major component. Through further manipulation of the systems using sol-gel chemistry, the morphology of the M-Si composites can be precisely controlled. Some of the properties of the resulting materials that can be tailored to specific applications include particle sizes, porosity, the degree of mixing, and the composition to name a few.

Clapsaddle, B. J. *et. al.* *J. Non-Cryst. Solids*, 2003, *331*, 190.

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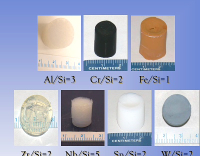
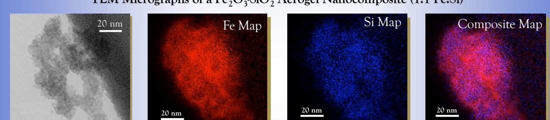
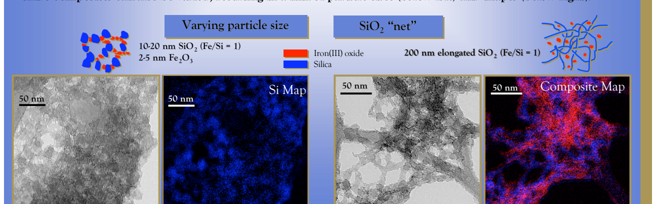


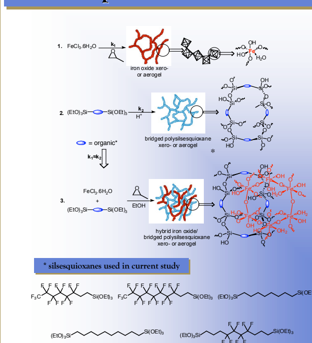
TEM Micrographs of a Fe_2O_3-SiO_2 Aerogel Nanocomposite (1:1 Fe:Si)



Energy filtered transmission electron microscopy shows good mixing of the Fe_2O_3 and SiO_2 phases on the nanoscale (above). Other M-Si mixed oxide systems show the same degree of mixing. Morphologies of the mixed oxide composites can also be varied, resulting in a mix of particle sizes (below left) and shapes (below right).

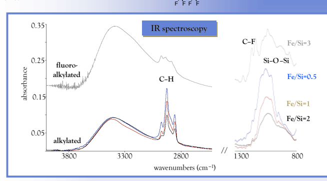


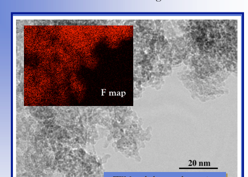
Composite Materials



Inorganic–Organic Interpenetrating Networks (IPN's)

The integration of inorganic oxides with organics at nanometer length scales can extend the range of physical, mechanical, and chemical properties that can be obtained with simple mixtures of pure phases. To achieve mixing at these length scales, several strategies may be employed. One method involves the formation of interpenetrating networks (IPNs) . IPNs may be assembled either sequentially or simultaneously, as shown to the left. The simultaneous formation of two or more interpenetrating networks is the most efficient. The objective of this research is to develop methods for preparing monoliths of iron oxide and silsesquioxane networks incorporating hydrocarbon or fluorocarbon groups as an integral part of the matrix. The organic component can be used to induce organization and/or long-range order, to modulate the mechanical properties, or enhance more specialized applications, such as their use as energetic materials. For these as well as other applications, it is desired that both the inorganic and organic components be "mixed" at nanometer length scales.





TEM and elemental mapping

According to the characterization results for the nanostructures, as well as the physical properties of the materials, the IPNs exhibited a uniform dispersion of both components with no evidence for phase separation on length scales > 5nm. It is believed that this methodology is general to the preparation of a large variety of transition and main group metal hybrid composites.

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